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Gas chromatograph with downstream mass spectrometer and method for gas chromatographic mass spectrometric analysis of a substance mixture

For gas chromatographic analysis of a substance mixture this mixture is directed together with a carrier gas through a chromatographic separation device in which the substances of the substance mixture are separated as a result of their different retention times and thus appear one after the other at the output of the separation device. Different detectors, such as heat conductivity detectors or flame ionization detectors for example, are available for the detection of the separated materials. The use of a mass spectrometer as detector also makes it possible, in addition to detecting the chromatographically separated materials, to differentiate between materials with the same retention times but different masses. Since the mass spectrometric analysis of materials is undertaken in a vacuum, the presence of the carrier gas which comes out of the gas chromatograph together with the separated materials is undesired. The mass spectrometer is thus connected via a controllable inlet valve to the output of the separation device, said inlet valve only being opened on demand, that is on arrival of the separated materials, with the carrier gas being removed as well (DE 1598568). Although it is possible to detect in the removed carrier gas the arrival of the separated substance mixture and to open the inlet valve as a function of this event, a part of the separated material, namely that material removed at the start with the carrier gas, is lost to mass spectrometric analysis in this case. The control of the feeding of separated materials to the mass spectrometer can thus only be undertaken in a relatively crude manner by adhering to safety times, so that a not insignificant amount of carrier gas gets into the mass spectrometer and a correspondingly high pump power is required to generate the

necessary vacuum.

The underlying object of the invention is thus to optimize the mass spectrometric analysis of gas chromatographically separated materials.

5 In accordance with the invention the object is achieved by a gas chromatograph with a downstream mass spectrometer which is connected via a controllable inlet valve to the output of a separation device of the gas chromatograph separating the materials passing through it, with a detector detecting the
10 separated materials in a non-destructive manner being arranged between the output of the separation device and the inlet valve in-line and an evaluation device being arranged downstream from the detector which evaluates the detector signals generated by the detector and, depending on these signals, controls the
15 inlet valve to introduce predetermined materials into the mass spectrometer.

The object is further achieved by a method for gas chromatographic mass spectrometric analysis of a substance mixture, which, for separation of the materials contained in
20 it, is directed by means of a carrier gas through a separation device, at the output of which the separated materials arriving there are introduced for quantitative determination via a controllable inlet valve into a mass spectrometer, with the separated materials being detected by a detector arranged in-
25 line between the output of the separation device and the inlet valve, and depending on the detection, the inlet valve is controlled for introduction of predetermined materials into the mass spectrometer.

The separated materials appearing at the output of the
30 separation device are detected in-line and non-destructively, with only those materials being forwarded to the mass

spectrometer which have been selected for a further mass spectrometric analysis. As a result of the speed of the carrier gas stream the time taken by the materials to pass from the detector to the inlet valve of the mass spectrometer is known, so that the materials can be transferred very selectively to the mass spectrometer and thus the amount of carrier gas entering the mass spectrometer is minimal. The pump power for creation of the vacuum in the mass spectrometer can thus be correspondingly small, so that very small pumps, e.g. ion getter pumps, can be employed. This produces benefits as regards costs, service life, maintenance requirements and power consumption. Further the scope of measurement signal evaluation in the mass spectrometer is restricted just to the materials fed selectively to it, so that its electronics and software can be designed to be cheaper and more powerful (fast).

Materials which are not selected for mass spectrometric analysis can if necessary still be analyzed by the in-line detector and the downstream evaluation unit.

The only detectors employed are those which do not destroy the substance mixture, i.e. a suitable heat conductivity detector, optical detector or detector operating with surface acoustic waves for example. In order not to adversely affect the separation performance of the separation device, the measurement path through which the substance mixture flows in this case is preferably embodied by the detector such that its cross sectional dimensions correspond at least approximately to the cross sectional dimensions of the separation device.

In accordance with a preferred embodiment of the inventive gas chromatograph mass spectrometer the detector consists of a heat conductivity detector with heat resistors arranged in a bridge circuit, of which two heat resistors lying diagonally opposite one another in the two different halves of the bridge circuit

are arranged in the measurement path; the two other heat resistors then lie for example in a reference path through which the carrier gas flows.

For further explanation of the invention reference is made
5 below to the Figures of the drawing; The individual Figures show

Figure 1 an exemplary embodiment of the inventive gas chromatograph mass spectrometer and

Figure 2 an exemplary embodiment for the detector.

10 Figure 1 shows a gas chromatograph 1 with a downstream mass spectrometer 2 for analysis of a substance mixture (sample) 3, which is fed, after being taken out of a technical process and prepared, to a dosing device 4. The dosing device 4 is used to
15 amount of the sample 3 in the form of a short and precisely limited sample drop 5 into a carrier gas stream 6 and feed it to a separation device 7 in the form of a separation column or separation column circuit. The separation device 7 separates the materials contained in the sample drop 5 in accordance with
20 their retention periods, so that the materials appear at the output of the separation device 7 in turn.

A detector 8 for detecting the separated materials is arranged at the output of the separation device 7. The detector 8 delivers a detector signal 9 which contains a peak 10 for each
25 separated material, the surface of said peak being proportional to the amount of material. In an evaluation unit 11 arranged downstream from the detector 8, the arrival of selected materials is determined on the basis of their peaks 10 and, depending on this event and on the carrier gas speed, an inlet
30 valve 12 between the detector 8 and the mass spectrometer 2 is controlled such that this valve only introduces the selected

materials into the mass spectrometer 2 and removes the other materials as well as the carrier gas via an outlet 13.

The selected materials arriving in the vacuum 14 of the mass spectrometer 2 are ionized in a zone source 15, then separated
5 in a mass filter 16 in accordance with their mass/charge ratio and finally verified by means of a detector array 17 with downstream evaluation device 18.

Figure 2 shows an example of the in-line detector 8 which is embodied in this diagram as a heat conductivity detector. The
10 detector 8 features wire-wound heat resistors 20, 21, 22, 23 arranged in a bridge circuit 24, with the bridge circuit 24 being fed at two opposite circuit points 25 from a detector circuit 26 with a current, and the voltage of the detector circuit 26 occurring between the two other opposing circuit
15 points 27 being recorded for generation of the detector signal. The heat resistors 20 and 21 lying diagonally opposite one another in the bridge circuit 24 are arranged between the separation device 7 and the inlet valve 12 in a measurement path 28 of the detector 8, while the two remaining heat
20 resistors 22 and 23 are arranged in a reference path 29 through which the carrier gas 6 flows. The measurement path 28 is embodied such that its internal cross-sectional dimensions correspond to those of the connected separation device 7, so that the separated substance mixture flowing through it is not
25 destroyed. The heat resistors 20, 21, 22, 23 and the inner walls of the paths 28, 29 are made of materials which behave in an inert way in relation to the substance mixture to be analyzed or to the support gas 6, for example gold or silicon dioxide (quartz), so that a change in the substance mixture as
30 a result of chemical reactions is excluded.